KINETICS AND MECHANISM OF Ir (III) CATALYSED POTASSIUM BROMATE OXIDATION OF SOME ORGANIC COMPOUNDS

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KUM KUM DIXIT

Under the supervision of

Dr. RAJ KISHOR SHUKLA
Head, Chemistry Department
ATARRA P. G. COLLEGE
ATARRA (BANDA)

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CERTIFICATE

This is to certify that the thesis entitled "Kinetics and Mechanism of I_r(III) catalysed Potassium Bromate Oxidation of Some Organic Compounds" submitted for the degree of Doctor of Philosophy of Bundelkhand University, Jhansi (U.P.) is a record of bonafide research work carried out by Kum Kum Dixit under my guidance and supervision.

The work embodied in this thesis or a part thereof, has not been submitted for the award of any other degree or diploma. All the help and assistance received during the course of present investigations have been duly acknowledged.

R.K. Shukla

Raj Kishor Shukla
M.Sc.Ph.D.
Head, Chemistry Department
Atarra P.G.College Atarra
(BANDA), U.P.

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Kum Kum Dixit

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CHAPTER I

INTRODUCTION

1 : INTRODUCTION

Mankind has been intrigued from the very beginning by oxidation processes such as burning wood, rusting of iron, fermentation of sugar etc. The study of the mechanism of redox processes is a subject of considerable importance from both inorganic and organic compound properties points of view. The study of reaction mechanism also helps in under standing the nature of life. The search of informations about the changes which compounds undergo is the very essence of chemistry not only because of the end products but in view of the intermediates and the transformations which controll the over all reaction. Chemists or engineers who must develop efficient synthetic procedures for practical purposes need to know the factors that influence rates of the reactions in order to proceed rationally with their work. The rate of chemical reaction and influence of various factors is the main concern of chemical kinetics. The molecular descriptions of reactive species are deduced and ascertained from reaction rate measurements and other scientific observations, and attempt is made to understand how individual transformations occur.

Although in a few cases, it is not possible to provide complete informations on the basis of kinetic studies, even then chemical kinetics is still supposed to provide the most powerful method of investigating the mechanism of a process, inspite of other techniques available to establish the reaction mechanisms. In most of the reactions the intermediates are

obtained, the identity of which cannot be explained on the basis of kinetic alone. Other methods such as E.S.R. techniques have to be applied to identify the end products formed on the completion of the reaction. Intermediates occur in most reaction sequence. The best evidence for an intermediate is its isolation and characterisation, although intermediates by their very nature are often too reactive to be isolated.

It is not often simple to interpret the experimentally determined rate law in terms of the reaction mechanism, as an alternative mechanisms may lead to the same rate law. Another difficulty in the interpretation of experimental rate law in terms of mechanism in the case of reactions in solution is caused by the possible participation of solvent in the mechanism, since the solvent concentration may not be altered significantly, its effect on rate law and hence the involvement in mechanism is completely unknown in most cases. No doubt, significance advance has been made in the matter of correlating the dielectric constant of the medium with the rate of various types of the reactions, but the ideas about the microscopic dielectric constant in the immediate vicinity of a reactant particle, the existence, extent and nature of selective solution, the effect of solvation on electron distribution and reactivity of reactant particles and other factors in solvent effects remain vague.

Laideler[1] has reported that ion - dipole activated complexes have complicated distribution of charges so that specific

hydration plays an important role. He is of the opinion that in solvent rate theories dielectric saturation should be taken into account, the solvent still being treated as continuous. In spite of these difficulties, it has been possible to explain many reactions by a set of simple processes which are found in reasoning and are in accordance with experience and therefore, we accept them essentially true and correct. The problem of analysing the rate of chemical reactions in solution from the molecular point of view seems rather complex. The reason is that, in solutions, any particular molecule is, at any moment, in close contact with a number of nearest neighbours which may vary in number from four to twelve. Intimate mechanical motions of the atom and electrons belonging to the molecule (or a pair of molecule) undergoing chemical reactions are thus being constantly intruded upon in a random and arbitrary way by a impossible large number of neighbouring molecule.

Interactions of the neighbouring molecules are sufficiently large in the case of reactions involving ionic species and hence form an integral part of the scheme. The importance of the solvent interactions may be realised from the observations noted from amongst thousands of reactions which have been studied in gas phase. The study of the ionic reactions has been more or less restricted to solutions for the obvious reasons that ionic species are virtually non existent in the gaseous phase. The most thoroughly investigated reactions in solution are the electron

transfer reactions between an oxidant and a reductant[2]. Strictly, speaking the electron transfer reactions are the inorganic ones while most of the carbonic redox systems involve transfer of an atom or ion[3]. The study of radio active exchange between two species of different oxidation states with no net chemical reactions have supported the atom or ion transfer mechanism. Most of the recent works have shown that among the organic redox systems, also the electron transfer is by no means the only, nor even the favoured route by the powerful oxidising agents such as permanganate, chromic acid and vanadium (V) etc. Several oxidising agents have been used for the overall as well as step by step oxidation purpose. The common oxidants used for oxidation of organic materials are potassium permanganate and potassium dichromate glycols have earlier been used as reducing agent by Singh and Coworkers[4] for kinetic investigations in alkaline medium with potassium hexacyanoferrate (III) as oxidising agent. Singh and Singh[5] have studied the oxidation of diethylene glycol, methyl diethylene glycol, ethyl diethylene glycol and butyl diethylene glycol by acidic solution of N-bromoacetamide in the presence of Ru(III) chloride as catalyst. In above investigations, it was observed that after 15 to 20% reaction has proceeded a pale yellow colour is developed which is ascribed due to bromine formation in the reaction. The bromine thus formed in the reaction sets a parallel oxidation process and thus it was not possible to determine the exact order of reaction with respect to reactive species and hence they eliminated the bromine formed in the

reaction by using mercuric acetate as bromide ion scavenger. They observed that there was difference in the velocity of reactions with and without the use of mercuric acetate. This confirmed that unless bromineáis eliminated from the reaction field the kinetic order in NBA oxidation of glycols was not correct. Hence they investigated these reactions in the presence of mercuric acetate. They have observed first - order kinetics with respect to N-bromoacetamide, H^+ ion and Ru(III). They have also observed that in low concentration range of glycols the order of the reaction with respect to glycols is one while first - order tends to shift to zero - order at higher concentration ragne of glycols.

N-Bromosuccinimide oxidation of some glycols e.g. diethylene glycol and ethyl diethylene glycol in perchloric acid media in the presence of mercuric acetate as Br^- scavenger and using Ru(III) chloride at catalyst has been studied from kinetic and mechanistic points of view by Singh et al[6,7]. First-order dependence of these reactions on each of reactants i.e. N-bromosuccinimide, glycol, Ru(III) and H^+ has been observed by them. They have also showed a solvent isotope effect. They have showed that N-bromosuccinimide forms a complex with Ru(III) chloride reactive species and the complex thus formed interacts with protonated glycol in a slow and rate controlling step.

1.1 : POTASSIUM BROMATE AS OXIDANT

In acidic media potassium bromate has been reported to be a powerful oxidant with the redox potential of 1.44 volt. It has been widely used in the oxidation of alcohols[8], cyclanols[9,10], phenols[11], α- hydroxy acids[12], aldehydes[13-15], tartaric acid[16], some labile substrates and nitrites[18].

S.C.Pati and M.Mishra[19] have reported potassium bromate as oxidant in oxidation of phenols in presence of mercuric acetate. Bromate has also been reported as oxidant by Radhakrishnamurthi et al[20] in oxidation of nitrite in presence of ruthenium(III) chloride as catalyst. Ru(III) catalysed oxidation of dimethylsulphoxide with bromate[21] and iodate ions has also been investigated by Radhakrishnamurthi and Sahu. Singh et al[22] have reported recently oxidation of some glycol and cyclic alcohols by solution of potassium bromote.

Inspite of good amount of work on potassium bromate oxidations there are still scope. In the present thesis an attempt has been made to obtain the kinetic informations on Ir(III) chloride catalysed oxidation of a few amino acids by acidic solution of potassium bromate. The kinetic data have been used to elucidate the reaction mechanisms of aforesaid reactions.

1.2 : SUMMARY OF KINETIC RESULTS OBTAINED IN Ir(III) CHLORIDE CATALYSED OXIDATIONS OF AMINO ACIDS BY ACID SOLUTION OF POTASSIUM BROMATE

The kinetic observations noted in oxidation of alanine, phenylalanine and valine by potassium bromate in presence of iridium trichloride as catalyst and mercuric acetate as Br^- scavenger in perchloric acid are summarised below :

(1) The reaction between potassium bromate and amino acids under the experimental conditions employed here shows zero - order kinetics in potassium bromate.

(2) Oxidation of alanine, phenyl alanine and valine by potassium bromate shows first order dependence on each of the amino acids used.

(3) Zero-order dependence of the title reactions on H^+ was observed.

(4) First-order kinetics with respect to iridium(III) chloride in p otassium bromate oxidation of amino acids used here was obsefved.

(5) Insignificant effect of variation of mercuric acetate concentration on reaction rate was observed.

(6) Negligible effect of addition of potassium chloride on the reaction rates for the title reactions was noted.

(7) Change in ionic strength of the medium did not influence the oxidation of amino acids by potassium bromate.

(8) Increase in temperature increased the reaction rates significantly.

The above results have been interpreted and finally rate law has been derived on the basis of proposed mechanism.

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CHAPTER II

CHEMICALS, PREPARATION OF THEIR SOLUTIONS AND STOICHIOMETRY

2.1 : CHEMICALS USED AND PREPARATION OF THEIR SOLUTIONS

Potassium bromate of B.D.H., A.R. grade was used and its aqueous solution was prepared by dissolving its sample in definite volume of double distilled water. The solutions of alanine, phenylalanine and valine (all E. Merck) were prepared by dissolving the required weighed samples.

Sodium perchlorate and perchloric acid (60%) of E.Merck (F.R.G.) grade were used for preparing their solutions. E Merck (Germany) grade of mercuric acetate was used for preparing the solution of mercuric acetate in 10% (V/V) acetic acid (E.Merck).

The solution of iridium trichloride (Johnson & Matthey) was prepared by dissolving its 1 gm sample in hydrochloric acid of known strength and its strength was maintained at 10.00 x 10^{-4}M in 0.02 N HCl. The solution of sodium thiosulphate was standardised against standard solution of copper sulphate iodometrically.

Standard solution of KCl (BDH, A.R.) was prepared by dissolving its desired amount in double distilled water. One percent starch solution was always prepared afresh.

2.2 : PROCEDURE

The reaction stills blackened from outside were used so as to eliminate the photochemical reactions. Desired amounts of reactants i.e. reducing amino acids, perchloric acid, mercuric acetate, sodium perchlorate (where ever necessary), iridium trichloride etc. except potassium bromate were taken in a reaction vessel and was kept in a thermostatic water bath maintained at the temperature of the experiment within $\pm$ 0.1°C accuracy. After allowing for sufficient time for substances to attain the desired temperature, requisite amount of potassium bromate solution (also maintained at the same temperature) was rapidly mixed with solutions of reaction vessel and vigorously shaken. At suitable intervals of time, a known amount of reaction mixture (5 ml) was taken out and amount of unreacted potassium bromate was estimated iodometrically.

2.3 : CALCULATION METHOD

The kinetic data were obtained from above estimations at different time intervals. (a - x) i.e. remaining amount of potassium bromate were plotted against time for different sets of reaction. Initial velocity constant i.e. $(-dc/_{dt})$ was calculated from the slope on the curve of above plots. The slope was drawn at about $KBrO_3^*$ corresponding to time 10 minutes when reactions have hardly proceeded about 10 to 20%. Thus from $(-dc/_{dt})$ values at different $KBrO_3$, order with respect to reactants was determined.

If $(-dc/_{dt})$ values at different $KBrO_3$ are nearly constant, the reaction is zero - order with respect to bromate. If $(-dc/_{dt})/[KBrO_3]^*$ values are constant, the reaction is first - order in bromate (where $[KBrO_3]^*$ is the concentration of bromate at which $(-dc/_{dt})$ was plotted). Once the order with respect to potassium bromate is determined, the order with respect to other species is also easily determined which have been described in the following chapters in details.

2.4 : STOICHIOMETRY AND PRODUCTS ANALYSIS

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing on excess of bromate over amino acids (in different ratios) at 35^{o}C for 48 hours. Estimation of unconsumed bromate in different sets showed that one mole of amino acid consumed one mole of bromate and accordingly the stoichiometric equation may be written as (1).

$$RCH(NH_2)COOH + HBrO_3 \longrightarrow$$

$$RCHO + NH_3 + CO_2 + HBrO_2 \qquad \text{.... (1)}$$

where R stands for $-CH_3$, $C_6H_5CH_2-$ and $(CH_3)_2CH$ in alanine, phenyl alanine and valine respectively. Here $KBrO_3$ exists as $HBrO_3$ in acidic medium.

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CHAPTER III

DETERMINATION OF ORDER OF REACTION WITH RESPECT TO POTASSIUM BROMATE IN OXIDATION OF SOME AMINO ACIDS

3 : DETERMINATION OF ORDER OF REACTION WITH RESPECT TO POTASSIUM BROMATE IN OXIDATION OF SOME AMINO ACIDS

This chapter describes the study of determination of the order of the reaction with respect to potassium bromate which has been used in the present investigation as an oxidant in oxidation of a few amino acids, namely alanine, phenyl alanine and valine in the presence of iridium (III) chloride as catalyst in acidic media. In the beginning, it was observed after 15 to 20 minutes that the yellow colour is developed in the reaction mixture, which was due to formation of bromine. It was observed that the slow reaction proceeding in the beginning became faster after some time, indicating setting up of parallel bromine oxidation probably. When mercuric acetate was initially added in the reaction mixture the yellow colour appearance was stopped and the reaction also proceeded smoothly from beginning to the last. Mercuric acetate infact acted here as bromide ion scavenger and it eliminates bromide ion which was producing bromine on interaction with potassium bromate. Hence all experiments were carried out in the presence of mercuric acetate. Preliminary investigations also showed

that there is no effect of change in ionic strength of the medium on rate of the reaction. Here experiments were performed without keeping ionic strength of the medium constant.

In order to investigate the order of the reactions with respect to potassium bromate, various experiments with different concentrations of potassium bromate but at fixed concentrations of all other reactants were carried out. All experiments have been carried out under isolation conditions i.e. in all reactions concentration of potassium bromate has always been kept comparatively much smaller than that of substrates, i.e. amino acids. The results of various experiments carried out in oxidation of alanine, phenylalanine and valine have been given in tables 3.1 - 6, 3.7 - 3.12 and 3.13 - 3.18, respectively. For the sake of convenience Ir(III) has been written for iridium(III) chloride throughout the thesis. The value of $(-dc/_{dt})$ has been determined by the method described in 2nd chapter.

TABLE 3.1

$[KBrO_3] = 3.34 \times 10^{-3}$M, $[HClO_4] = 1.00 \times 10^{-2}$M,

$[\text{Alanine}] = 3.32 \times 10^{-2}$M, $[\text{Ir(III)}] = 1.92 \times 10^{-5}$M

$[\text{Hg}\ (\text{OAc})_2] = 4.00 \times 10^{-3}$M, Temp. 35^{o}C

Time (min.)	Volume of hypo solution (4.24×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ $ML^{-1}\ s^{-1}$
0	19.62	
10	18.06	
20	17.18	
30	16.84	
40	16.50	3.36
55	14.60	
70	14.18	
85	13.78	
115	13.46	
150	12.76	

TABLE 3.2

$[KBrO_3] = 2.25 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[\text{Alanine}] = 3.32 \times 10^{-2} M$, $[Ir(III)] = 1.92 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution (2.78×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\,L^{-1}\,s^{-1}$
0	20.00	
5	18.84	
10	18.42	
15	18.04	
30	16.64	3.12
45	15.52	
60	14.46	
75	13.56	
100	11.26	
135	9.98	
195	8.58	

TABLE 3.3

$[KBrO_3]$ = 1.34×10^{-3}M, $[HClO_4]$ = 1.00×10^{-2}M

[Alanine] = 3.32×10^{-2}M, [Ir(III)] = 1.92×10^{-5}M

$[Hg(OAc)_2]$ = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.36×10^{-3}M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	24.28	
5	21.72	
10	20.76	
15	19.68	
20	18.64	
25	16.48	3.30
35	15.80	
50	12.98	
65	10.90	
80	8.62	
95	7.92	

TABLE 3.4

$[KBrO_3]$ = 1.00×10^{-3} M, $\cancel{[HClO_4 M}$, $[HClO_4]$ = 1.00×10^{-2} M

$[\text{Alanine}]$ = 3.32×10^{-2} M, $[Ir(III)]$ = 1.92×10^{-5} M

$[Hg(OAc)_2]$ = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.35×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	18.26	
5	15.50	
10	14.00	
15	13.26	
25	11.16	3.28
40	9.00	
55	7.38	
70	5.86	
85	4.62	
100	3.88	

TABLE 3.5

$[KBrO_3] = 0.80 \times 10^{-3}$M, $[HClO_4] = 1.00\times10^{-2}$M

$[\text{Alanine}] = 3.32 \times 10^{-2}$M, $[Ir(III)] = 1.92\times10^{-2}$M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$M, Temp. 35°C

Time (min.)	Volume of hypo solution solution (1.25×10^{-3}N) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	16.40	
5	14.18	
10	12.76	
15	11.74	
25	8.40	3.08
40	6.68	
55	5.42	
70	4.64	
85	4.36	
100	3.82	

TABLE 3.6

$[KBrO_3] = 0.67 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[\text{Alanine}] = 3.32 \times 10^{-2} M$, $[Ir(III)] = 1.92 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$ and Temp. 35^0C

Time (min.)	Volume of hypo solution ($1.20 \times 10^{-3}N$) in ml	$(-\frac{dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	13.80	
5	10.20	
10	8.46	
15	7.12	
20	6.14	
25	5.52	3.26
30	5.00	
35	4.86	
45	4.44	
60	4.00	
75	3.68	

TABLE 3.7

$[KBrO_3] = 3.34 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

[Phenyl alanine] $= 5.00 \times 10^{-2}$ M, $[Ir(III)] = 1.92 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$, Temp. 35°C

Time (min.)	Volume of hypo solution (3.36×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	25.10	
5	24.22	
10	23.08	
25	22.18	
40	21.32	2.98
70	19.24	
100	17.10	
130	14.66	
160	12.38	
190	9.86	
220	7.46	

TABLE 3.8

$[KBrO_3] = 2.25 \times 10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[\text{Phenylalanine}] = 5.00\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp.35°C

Time (min.)	Volume of hypo solution ($3.00\times10^{-3}N$) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	18.52	
5	17.46	
10	16.12	
20	15.52	
30	14.80	2.88
60	11.82	
90	9.76	
120	7.82	
150	5.96	
180	5.02	

TABLE 3.9

$[KBrO_3] = 1.34\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

[Phenylalanine] = $5.00\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. 35°C

Time (min.)	Volume of hypo solution ($2.86\times10^{-3}N$) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\,L^{-1}\,s^{-1}$
0	11.60	
5	10.98	
10	10.40	
20	9.72	
30	9.14	2.78
45	8.06	
60	6.82	
80	5.96	
110	4.90	
140	4.20	

TABLE 3.10

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[Phenylalanine] = 5.00 \times 10^{-2} M$, $[Ir(III)] = 1.92 \times 10^{-5}$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution (2.50×10^{-3}N) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	10.00	
5	9.46	
10	8.80	
20	8.06	
30	7.24	2.72
45	5.96	
60	5.28	
90	4.20	
120	3.66	
150	3.00	

TABLE 3.11

[$KBrO_3$] = 0.80×10^{-3}M, [$HClO_4$] = 1.00×10^{-2}M

[Phenyl alanine] = 5.00×10^{-2}M, [Ir(III)] = 1.92×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution (2.50×10^{-3}M) in ml	$\left(\frac{-dx}{dt}\right) \times 10^7$ $M\ L^{-1} s^{-1}$
0	8.00	
5	7.58	
10	7.20	
25	6.48	
45	5.32	2.88
60	5.00	
75	4.40	
100	4.00	
125	3.62	
150	3.32	

TABLE 3.12

$[KBrO_3] = 0.67 \times 10^{-3}M$, $[HClO_4] = 1.00 \times 10^{-2}M$

$[\text{Phenyl alanine}] = 5.00 \times 10^{-2}M$, $[Ir(III)] = 1.92 \times 10^{-5}M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3}M$, Temp. 35°C

Time (min.)	Volume of hypo solution ($2.30 \times 10^{-3}N$) in ml	$(-dc/dt) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0	7.20	
5	6.98	
10	6.48	
25	5.82	
40	5.08	3.02
55	4.48	
70	4.00	
95	3.40	
110	3.16	
125	2.90	

TABLE 313

$[KBrO_3] = 3.34 \times 10^{-3}M$, $[HClO_4] = 1.00 \times 10^{-2}M$

$[Valine] = 3.34 \times 10^{-2}M$, $[Ir(III)] = 0.78 \times 10^{-5}M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3}M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution ($3.00 \times 10^{-3}N$) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	26.60	
5	25.80	
10	24.96	
25	22.32	8.86
40	20.92	
60	17.86	
80	15.60	
100	9.80	
120	6.32	

TABLE 3.14

[$KBrO_3$] = 2.25×10^{-3} M, [$HClO_4$] = 1.00×10^{-2} M

[Valine] = 3.34×10^{-2} M, [Ir(III)] = 0.78×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.33×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\,L^{-1}\,S^{-1}$
0	17.12	
5	16.02	
10	14.80	
20	13.62	
30	11.82	
40	10.76	8.96
50	9.38	
65	8.62	
80	7.98	
100	7.00	

TABLE 3.15

$[KBrO_3] = 1.34 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[Valine] = 3.34 \times 10^{-2}$ M, $[Ir(III)] = 0.78 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.33×10^{-3} N) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	10.40	
5	8.96	
10	7.82	
15	6.66	
20	6.00	8.84
25	5.48	
30	5.02	
35	4.56	
40	4.00	
50	3.52	

TABLE 3.16

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M,

$[Valine] = 3.34 \times 10^{-2}$ M, $[Ir(III)] = 0.78 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.33×10^{-3}N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	8.12	
5	6.20	
10	5.40	
15	4.80	
20	3.38	9.10
25	4.20	
30	3.86	
40	3.54	
50	3.08	
60	2.82	

TABLE 3.17

$[KBrO_3]$ = 0.80×10^{-3} M, $[HClO_4]$ = 1.00×10^{-2} M

$[Valine]$ = 3.34×10^{-2} M, $[Ir(III)]$ = 0.78×10^{-5} M

$[Hg(OAc)_2]$ = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution solution (3.33×10^{-3} N) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ S^{-1}$
0	6.40	
5	5.02	
10	4.00	
15	3.52	
20	3.08	8.86
30	2.76	
40	2.50	
50	2.26	
60	2.00	

TABLE 3.18

$[KBrO_3] = 0.67\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[Valine] = 3.34\times10^{-2}M$, $[Ir(III)] = 0.78\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. 35^oC

Time (min.)	Volume of hypo solution ($1.68\times10^{-3}N$) in ml	$(\frac{-dc}{dt}) \times 10^{-7}$ $M\ L^{-1}\ s^{-1}$
0	9.64	
5	8.72	
10	6.92	
15	6.20	
25	5.40	9.28
40	4.56	
60	3.84	
80	3.44	
100	3.00	
120	2.56	

TABLE 3.19

[Alanine] = 3.32×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[Ir(III)] = 1.92×10^{-5} M, [$Hg(OAc)_2$] = 4.00×10^{-3} M

temp. 35°C

[$KBrO_3$] × 10^3 M	[$KBrO_3$]* × 10^3 M	($\frac{-dc}{dt}$) × 10^7 M L^{-1} s^{-1}
3.34	3.00	3.36
2.25	2.00	3.12
1.34	1.00	3.30
1.00	0.80	3.28
0.80	0.66	3.08
0.67	0.50	3.26

* concentration of potassium bromate at which ($\frac{-dc}{dt}$) was determined.

TABLE 3.20

[Phenylalanine] = 5.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[Ir(III)] = 1.92×10^{-5} M, [$Hg(OAc)_2$] = 4.00×10^{-3} M

Temp. 35°C

[$KBrO_3$] x 10^3 M	[$KBrO_3$]* x 10^3 M	($\frac{-dc}{dt}$) x 10^7 M L^{-1} s^{-1}
3.34	3.00	2.90
2.25	2.00	2.88
1.34	1.00	2.78
1.00	0.80	2.72
0.80	0.67	2.88
0.67	0.50	3.02

TABLE 3.21

[Valine] = 3.34×10^{-2}M, [$HClO_4$] = 1.00×10^{-2} M

[Ir(III)] = 0.78×10^{-5}M, [Hg$(OAc)_2$] = 4.00×10^{-3} M

Temp. 35°C

[$KBrO_3$] $\times 10^3$ M	[$KBrO_3$]* $\times 10^3$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
3.34	3.00	8.86
2.25	2.00	8.96
1.34	1.00	8.84
1.00	0.80	9.10
0.80	0.57	8.86
0.67	0.50	9.28

An examination of data of tables 3.19, 3.20 and 3.21 clearly indicate that the values of $(-dc/dt)$ remain constant at all concentrations of potassium bromate, which suggests that order of the reaction with respect to potassium bromate in oxidation of alanine, phenyl alanine and valine in acidic medium in the presence of iridium(III) chloride is zero.

CHAPTER IV

DETERMINATION OF ORDER OF REACTIONS WITH RESPECT TO AMINO ACIDS USED HERE WITH POTASSIUM BROMATE AS OXIDANT

4 : DETERMINATION OF ORDER OF REACTIONS WITH RESPECT TO AMINO ACIDS USED HERE WITH POTASSIUM BROMATE AS OXIDANT

This chapter describes the procedure to determine the order of the reaction with respect to amino acids used here. In order to obtain the dependence of the reaction on each amino acid, a number of experiments with varying concentrations of each amino acid at fixed concentrations of all other reactants have been carried out under the isolation conditions. The values of ($\frac{-dc}{dt}$) i.e. zero - order rate constant in potassium bromate is determined by usual method as described in chapter 2. It is observed that ($-dc/dt$) value in oxidation of each amino acids increases linearly with increase in the concentration of amino acids. The experimental data observed are recorded in tables 4.1 - 4.6, 4.7 - 4.12 and 4.13 - 4.18 in oxidation of alanine, phenyl alanine and valine respectively.

TABLE 4.1

[Alanine] = 1.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.28×10^{-3} N) in ml	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}
0	19.56	
5	18.76	
20	17.78	
40	16.28	0.82
60	15.46	
80	14.74	
100	13.80	
140	12.96	
160	12.54	
200	11.80	

TABLE 4.2

[Alanine] = 1.66×10^{-2} M, $[HClO_4]$ = 1.00×10^{-2} M,

[Ir(III)] = 1.92×10^{-5} M, $[KBrO_3]$ = 1.00×10^{-3} M

$[Hg(OAc)_2]$ = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.28×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right)\times10^7$ M L^{-1} s^{-1}
0	19.56	
5	18.72	
10	18.14	
15	17.64	
30	16.32	1.34
45	15.22	
60	14.16	
90	12.68	
120	11.10	
160	10.30	
200	9.22	

TABLE 4.3

[Alanine] = 2.50×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.56×10^{-3} M) in ml	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}
0	16.00	
5	15.64	
15	14.82	
25	13.34	1.96
35	12.64	
45	11.88	
75	9.92	
105	8.80	
135	7.76	
175	6.96	

TABLE 4.4

[Alanine] = 5.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 30°C

Time (min.)	Volume of hypo solution (1.56×10^{-3} N) in ml	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}
0	16.00	
5	15.00	
10	13.12	
15	11.82	
20	11.06	4.08
25	10.00	
30	9.30	
45	7.00	
60	5.66	
75	5.00	
90	4.32	

TABLE 4.5

[Alanine] = 7.50×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.56×10^{-3} M) in ml	$(-dc/dt)\times10^{7}$ M L^{-1} s^{-1}
0	16.00	
5	14.82	
10	13.00	
15	11.62	
20	10.82	5.88
25	9.78	
30	9.00	
45	6.65	
60	6.26	
75	4.80	
90	4.00	

TABLE 4.6

[Alanine] = 10.00×10^{-2}M, [$HClO_4$] = 1.00×10^{-2}M

[$KBrO_3$] = 1.00×10^{-3}M [Ir(III)] = 1.92×10^{-3}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.56×10^{-3}N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^{-7}$ $M\ L^{-1}\ s^{-1}$
0	16.00	
5	13.06	
10	11.48	
15	10.26	7.96
20	9.08	
25	3.26	
30	7.40	
35	6.48	
40	5.86	
50	5.10	

TABLE 4.7

[Phenylalanine] = 1.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 3.84×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (2.22×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	11.20	
5	10.40	
10	9.80	
15	9.50	
20	9.24	1.15
35	9.00	
50	8.76	
75	8.08	
100	7.46	
130	7.00	

TABLE 4.8

[Phenyl alanine] = 2.15×10^{-2}M, [$HClO_4$] = 1.00×10^{-2}M

[$KBrO_3$] = 1.00×10^{-3}M, [Ir(III)] = 3.84×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (2.22×10^{-3}M) in ml	$(\frac{-dc}{dt})\times10^{7}$ $M\,L^{-1}\,S^{-1}$
0	11.20	
5	9.60	
10	9.04	
15	8.64	
20	8.16	2.60
25	7.82	
30	7.52	
40	6.40	
50	5.86	
60	5.28	

TABLE 4.9

[Phenylalanine] = 3.34×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} , [Ir(III)] = 3.84×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hype solution (2.22×10^{-3} N) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\,L^{-1}S^{-1}$
0	11.20	
5	9.00	
10	8.64	
15	8.18	
20	7.68	4.06
25	7.02	
30	5.08	
40	4.48	
50	3.98	
60	3.42	

TABLE 4.10

[Phenylalanine] = 5.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 3.84×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solutions (2.22×10^{-3} M) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} S^{-1}
0	11.20	
3	9.06	
8	7.68	
15	5.86	
25	4.38	5.80
40	3.78	
55	3.10	
70	2.80	
85	2.32	

TABLE 4.11

[Phenyl alanine] = 7.50×10^{-2}M, $[HClO_4]$ = 1.00×10^{-2}M

$[KBrO_3]$ = 1.00×10^{-3}M, [Ir(III)] = 3.84×10^{-5}M

$[Hg(OAc)_2]$ = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (2.22×10^{-3}M) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\ L^{-1}\ s^{-1}$
0	11.20	
2	8.80	
5	6.96	
8	6.14	8.60
12	5.64	
18	5.00	
25	4.36	
40	3.86	
55	3.48	
70	2.66	

TABLE 4.12

[Phenyl alanine] = 10.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 3.84×10^{-5} M

[$Hg(OAc)_2$] = 4.08×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (2.22×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ M L^{-1} s^{-1}
0	11.20	
2	7.80	
5	6.50	
8	5.84	
12	5.30	11.60
18	4.60	
25	4.00	
40	3.60	
55	3.26	
70	2.46	

TABLE 4.13

[Valine] = 1.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.75×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	6.74	
2	5.80	
5	5.60	
10	5.22	
15	5.00	9.24
30	4.40	
45	3.88	
60	3.40	
75	3.02	
90	2.80	

TABLE 4.14

[Valine] = 2.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.80×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	14.96	
2	12.08	
4	11.28	
10	9.46	
15	7.86	
20	6.68	19.02
30	5.74	
40	5.12	
50	4.72	
60	4.32	

TABLE 4.15

[Valine] = 3.34×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.80×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	14.96	
2	11.92	
5	10.34	
10	8.82	
15	8.00	31.56
20	6.98	
30	6.00	
40	5.00	
50	4.62	
60	4.20	

TABLE 4.16

[Valine] = 5.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.15×10^{-3} N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	21.82	
2	17.92	
10	13.92	
20	11.36	
30	10.76	46.56
40	9.40	
60	8.46	
80	7.50	
100	6.68	

TABLE 4.17

[Valine] = 7.50×10^{-2}M, [$HClO_4$] = 1.00×10^{-2}M

[$KBrO_3$] = 1.00×10^{-3}M, [Ir(III)] = 1.92×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volumesof hypo solution (1.15×10^{-3}M) in ml	$(\frac{-dc}{dt})\times10^7$ M L^{-1} s^{-1}
0	21.82	
2	17.64	
10	13.56	
20	11.00	
30	10.52	70.00
40	9.12	
60	8.16	
80	7.20	
100	6.06	

TABLE 4.18

[Valine] = 10.00×10^{-2} M, [$HClO_4$] = 1.00×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.20×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^{-5}$ M L^{-1} s^{-1}
0	20.50	
2	14.46	
5	12.80	
10	12.00	
20	10.70	91.50
30	10.00	
40	9.38	
60	8.32	
100	5.92	

The results of tables 4.1 - 4.6, tables 4.7 - 4.12 and tables 4.13 - 4.18 have been summarised in tables 4.19, 4.20 and 4.21 respectively.

TABLE 4.19

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[Ir(III)] = 1.92 \times 10^{-5}$ M, $[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M

Temp. 35°C

$[Alanine] \times 10^2$ M	$(-\frac{dc}{dt}) \times 10^7$ M L^{-1} s^{-1}	$10^5 k_1$ s^{-1} $(-dc/dt)/[Alanine]$
1.00	0.82	8.20
1.66	1.34	8.07
2.50	1.96	7.84
5.00	4.08	8.16
7.50	5.88	7.84
10.00	7.96	7.96

Average value of k_1 = 8.01×10^{-5} s^{-1}

TABLE 4.20

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$,

$[Ir(III)] = 3.84\times10^{-5}M$, $[Hg(OAc)_2] = 4.00\times10^{-3}M$

Temp. 35°C

[Phenyl alanine] 10^2	$\left(\frac{-dc}{dt}\right)10^7$	$10^5\ k_1 = \frac{\left(\frac{-dc}{dt}\right)}{[\text{Phenylalanin}]}$ s^{-1}
1.00	1.15	1.15
2.25	2.60	1.16
3.34	4.06	1.22
5.00	5.80	1.16
7.50	8.60	1.13
10.00	11.60	1.16

Average value of $k_1 = 1.16 \times 10^{-5}\ s^{-1}$

TABLE 4.21

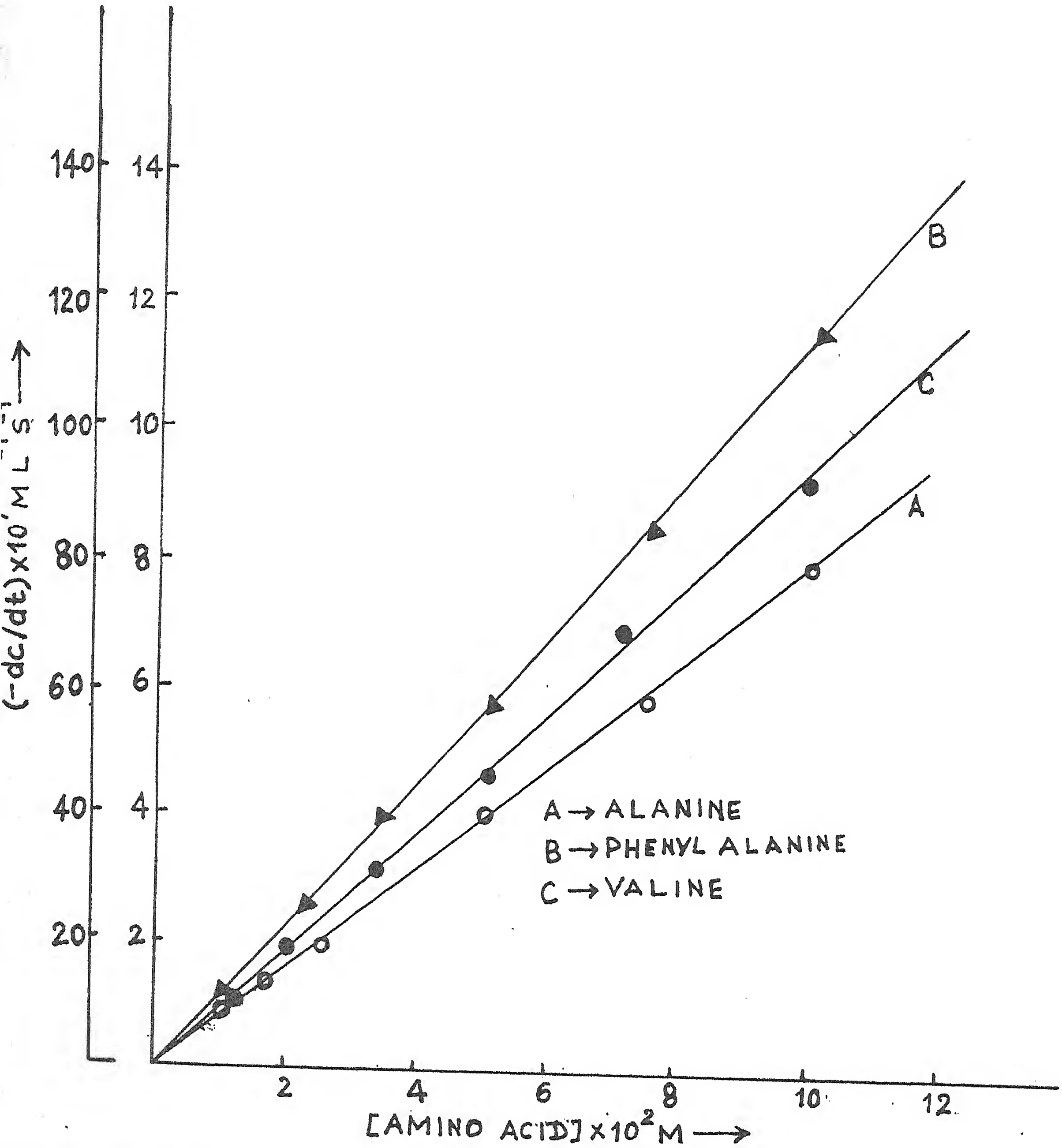
$[KBrO_3] = 1.00 \times 10^{-3}M$, $[HClO_4] = 1.00 \times 10^{-2}M$

$[Ir(III)] = 1.92 \times 10^{-5}M$, $[Hg(OAc)_2] = 4.00 \times 10^{-3}M$

Temp. 35°C

$[\text{Valine}] \times 10^2$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}	$10^5\ k_1 = \frac{(-dc/dt)}{[\text{valine}]}$ s^{-1}
1.00	9.24	9.24
2.00	19.02	9.51
3.34	31.56	9.47
5.00	46.56	9.31
7.30	70.00	9.30
10.00	91.50	9.15

Average $k_1 = 9.33 \times 10^{-5}\ s^{-1}$



i. 4.1: EFFECT OF [AMINO ACID] ON RATE AT 35°C.
$[BrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M,
(III)] $= 1.92 \times 10^{-5}$ M (A), 3.84×10^{-5} M (B) AND 1.92×10^{-5} M (C).

It is evident from the kinetic results of the summarised tables 4.19, 4.20 and 4.21 that on increasing the concentration of amino acid the value of zero - order rate constant i.e. ko or $(-dc/dt)$ value increases and the increase has been observed to be linear, showing first - order kinetics with respect to amino acid.

When a graph is plotted between $(-dc/dt)$ and [amino acid] a straight line is obtained whose slope (Fig. 4.1) gives the value of first - order constant (k_1). The close resemblance of k_1 values obtained from graphs and average k_1 from tables 4.19, 4.20 & 4.21 correspondingly clearly shows & confirms first order in amino acid.

CHAPTER V

DETERMINATION OF ORDER OF REACTION WITH RESPECT TO PERCHLORIC ACID IN OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

5 : DETERMINATION OF ORDER OF REACTION WITH RESPECT TO PERCHLORIC ACID IN OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

In this chapter an attempt has been made to investigate the order of the reaction with respect to perchloric acid in oxidation of amino acids employed here by potassium bromate in the presence of iridium(III) chloride. For obtaining this aim, a number of experiments with different consentrations of perchloric acidsat fixed concentrations of all other reactants have been performed and the results obtained have been recorded in tables 5.1 - 5.5, 5.6 - 5.10 and 5.11 - 5.15 in oxidation of alanine, phenyl alanine and valine respectively. Here also the value of $(-dc/_{dt})$ has been determined by the usual procedure described in 2nd chapter.

TABLE 5.1

[Alanine] = 5.00×10^{-2} M, [$HClO_4$] = 0.40×10^{-2} M

[$KBrO_3$] = 1.00×10^{-3} M, [Ir(III)] = 1.92×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.25×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	19.52	
5	15.90	
10	14.96	
15	14.10	
20	13.66	4.86
25	12.82	
35	11.56	
50	10.24	
65	8.86	
80	7.78	

TABLE 5.2

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 0.50 \times 10^{-2} M$

$[Alanine] = 5.00 \times 10^{-2} M$, $[Ir(III)] = 1.92 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution (1.25×10^{-3} N) in ml	$(\frac{dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	19.52	
5	15.70	
10	14.40	
15	13.26	
20	12.60	4.68
25	11.46	
35	9.96	
50	8.00	
65	6.82	
80	6.26	

TABLE 5.3

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 0.67×10^{-2}M

[Alanine] = 5.00×10^{-2}M, [Ir(III)] = 1.92×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.35×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	18.20	
2	16.56	
8	15.90	
15	14.58	
25	12.12	4.46
35	11.66	
50	10.26	
75	8.66	
100	7.06	

TABLE 5.4

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 2.00 \times 10^{-2}$ M

$[Alanine] = 5.00 \times 10^{-2}$ M, $[Ir(III)] = 4.00 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.25×10^{-3} N) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	19.52	
5	16.10	
10	15.02	
15	13.46	
20	11.94	4.66
25	11.06	
35	9.12	
50	6.48	
65	5.08	
80	4.24	

TABLE 5.5

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 4.00×10^{-2}M

[Alanine] = 5.00×10^{-2}M, [Ir(III)] = 1.92×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.25×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	19.32	
5	17.50	
10	16.08	
15	15.12	
20	14.62	4.63
25	13.84	
35	11.54	
50	9.06	
65	7.02	
80	5.05	

TABLE 5.6

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 0.40\times10^{-2}M$

$[\text{Phenyl alanine}] = 5.00\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution ($3.64\times10^{-3}N$) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\ L^{-1}\ S^{-1}$
0	6.92	
2	5.46	
5	4.72	
10	4.06	
15	3.72	2.90
20	3.38	
30	3.04	
45	2.76	
60	2.28	
80	1.90	

TABLE 5.7

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 0.50 \times 10^{-2} M$

$[\text{Phenyl alanine}] = 5.00 \times 10^{-2} M$, $[Ir(III)] = 1.92 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$ and Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution ($3.64 \times 10^{-3} N$) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0	6.92	
2	5.16	
5	4.80	
10	4.08	
15	3.84	2.88
20	3.40	
30	3.10	
45	2.68	
60	2.28	
80.	1.86	

TABLE 5.8

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 0.67\times10^{-2}M$

$[\text{Phenyl alanine}] = 5.00\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$ and Temp. 35°C

Time (min.)	Volume of hypo solution ($3.64\times10^{-3}N$) in ml	$(\frac{-dc}{dt})\times10^{7}$ $M\,L^{-1}\,s^{-1}$
0	6.92	
2	5.86	
5	5.40	
10	4.46	
15	3.62	2.94
20	3.04	
30	2.58	
50	2.36	
60	2.26	
70	2.10	

TABLE 5.9

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 2.00\times10^{-2}M$

$[\text{Phenyl alanine}] = 5.00\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution ($3.64\times10^{-3}M$) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\ L^{-1}\ s^{-1}$
0	6.92	
2	6.00	
5	5.68	
10	5.08	
15	4.62	2.86
20	4.14	
30	2.98	
40	2.48	
50	2.26	
65	2.00	
80	1.88	

TABLE 5.10

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 4.00 \times 10^{-2}$ M

[Phenyl alanine] = 5.00×10^{-2} M, [Ir(III)] = 1.92×10^{-5} M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.64×10^{-3}N) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	6.92	
2	6.08	
5	5.52	
10	5.02	
15	4.68	2.90
20	4.04	
30	3.68	
45	3.00	
60	2.38	
75	2.00	

TABLE 5.11

$[KBrO_3] = 1.00 \times 10^{-3}$M, $[HClO_4] = 0.40 \times 10^{-2}$M

$[Valine] = 3.34 \times 10^{-2}$M, $[Ir(III)] = 7.68 \times 10^{-6}$M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.34×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	8.40	
2	7.50	
5	6.40	
10	5.58	8.88
15	4.82	
25	3.86	
35	3.50	
50	3.08	
65	2.76	

TABLE 5.12

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 0.50 \times 10^{-2}$ M

$[Valine] = 3.34 \times 10^{-2}$ M, Temp. 35^{0}C

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, $[Ir(III)] = 7.68 \times 10^{-6}$ M

Time (min.)	Volume of hypo solution (3.34×10^{-3} N) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	8.40	
2	7.38	
5	6.64	
10	5.64	8.62
15	5.00	
25	4.18	
35	3.38	
50	3.02	
65	2.78	

TABLE 5.13

$[KBrO_3]$ = 1.00×10^{-3}M, $[HClO_4]$ = 0.67×10^{-2}M

[Valine] = 3.34×10^{-2}M; [Ir(III)] = 7.68×10^{-6}M

$[Hg(OAc)_2]$ = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.34×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	8.40	
2	7.46	
5	6.70	
10	5.68	8.82
15	4.98	
25	4.28	
35	3.42	
50	3.10	
65	2.70	

TABLE 5.14

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 2.00 \times 10^{-2}$ M

$[Valine] = 3.34 \times 10^{-2}$ M, $[Ir(III)] = 7.68 \times 10^{-6}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (2.25×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} S^{-1}
0	11.68	
2	9.94	
5	8.56	
10	7.58	
15	6.38	8.76
25	5.34	
35	4.52	
50	3.60	
65	2.68	

TABLE 5.15

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 4.00×10^{-2}M

[Valine] = 3.34×10^{-2}M, [Ir(III)] = 7.68×10^{-6}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, temp. 35°C

Time (min.)	Volumes of hypo solution (2.25×10^{-3}N) in ml	$(\frac{dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	11.68	
2	9.92	
5	8.60	
10	7.60	
15	6.36	8.80
25	5.32	
35	4.56	
50	3.62	
65	2.62	

The kinetic results of tables 5.1 - 5.5 & table 4.4 tables 5.6 - 5.10 and table 3.10 and tables 5.11 - 5.15 and table 3.16 have been summarised in tables 5.16, 5.17 and 5.18 in oxidation of alanine, phenyl alanine & valine, respectively.

TABLE 5.16

$[KBrO_3] = 1.00 \times 10^{-3}$M, $[Ir(III)] = 1.92 \times 10^{-5}$M

$[Alanine] = 5.00 \times 10^{-2}$M, $[Hg(OAc)_2] = 4.00 \times 10^{-3}$M

Temp. 35^{o}C

$[HClO_4] \times 10^2$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0.40	4.86
0.50	4.68
0.67	4.46
1.00	4.08
2.00	4.66
4.00	4.63

TABLE 5.17

$[KBrO_3] = 1.00\times10^{-3}$M, $[Ir(III)] = 1.92\times10^{-5}$M

[Phenyl alanine] = 5.00×10^{-2}M, Temp.35°C

$[Hg(OAc)_2] = 4.00\times10^{-3}$M

$[HClO_4] \times 10^2$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} S^{-1}
0.40	2.90
0.50	2.88
0.67	2.94
1.00	2.72
2.00	2.86
4.00	2.90

TABLE 5.18

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[Ir(III)] = 7.68 \times 10^{-6} M$

$[Valine] = 3.34 \times 10^{-2} M$, $[Hg(OAc)_2] = 4.00 \times 10^{-3} M$

Temp. $35^{o}C$

$[HClO_4]\ 10^2$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0.40	8.88
0.50	8.62
0.67	8.82
1.00	9.10
2.00	8.76
4.00	8.80

A careful examination of kinetic observations reported in summarised tables 5.16, 5.17 and 5.18 clearly indicates that on varying the concentrations of perchloric acid in oxidation of alanine, phenylalanine and valine the value of ($\frac{-dc}{dt}$) does not change appreciably. This shows that the order of the reaction with respect to perchloric acid is zero in all oxidation processes studied here. This further suggests that probably H^+ ions are involved in fast steps of the reaction mechanism which shall be discussed in last chapter.

CHAPTER VI

DETERMINATION OF ORDER OF REACTIONS WITH RESPECT TO IRIDIUM(III) CHLORIDE IN OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

6 : DETERMINATION OF ORDER OF REACTIONS WITH RESPECT TO IRIDIUM(III) CHLORIDE IN OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

In this chapter the main aim has been to determine the dependence of the reactions on the concentrations of iridium(III) chloride. In order to realise this aim a number of experiments with varying concentrations of iridium (III) chloride but at fixed concentrations of the remaining reactants have been carried out and the results of such experiments in oxidation of alanine, phenylalanine and valine have been recorded in tables 6.1 - 6.5, 6.6 - 6.10 and 6.11 - 6.15 respectively. Here in this chapter also the value of ($\frac{-dc}{dt}$) has been determined with usual procedure as described in 2nd chapter. All the reactions have been observed to be affected by increase in the concentrations of iridium(III), which is clear from the results of experiments recorded in tables 6.1 - 6.15. In each experiment value of $KBrO_3^{*}$ is taken at 0.80×10^{-3}M at which ($\frac{-dc}{dt}$) has been drawn.

TABLE 6.1

$[KBrO_3] = 1.00 \times 10^{-3}$M, $[HClO_4] = 1.00 \times 10^{-2}$M

$[Alanine] = 5.00 \times 10^{-2}$M, $[Ir(III)] = 0.78 \times 10^{-5}$M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.17×10^{-3}M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0	21.30	
5	18.94	
10	17.72	
15	17.02	
20	16.12	1.64
25	15.34	
35	14.20	
45	13.24	
60	11.52	
75	10.70	
90	9.86	
105	9.10	

TABLE 6.2

$[KBrO_3] = 1.00\times10^{-3}$M, $[HClO_4] = 1.00\times10^{-2}$M

$[Alanine] = 5.00\times10^{-2}$M, $[Ir(III)] = 1.35\times10^{-5}$M

$[Hg(OAc)_2] = 4.00\times10^{-3}$M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.17×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	21.30	
5	18.26	
10	16.10	
15	15.08	
20	13.76	
25	12.68	2.85
30	11.72	
40	9.68	
50	8.40	
60	7.48	
70	7.26	

TABLE 6.3

[$KBrO_3$] = 1.00×10^{-3} M, [$HClO_4$] = 1.00×10^{-2} M

[Alanine] = 5.00×10^{-2} M, [Ir(III)] = 1.55×10^{-5}

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.17×10^{-3} M) in ml	$(-\frac{dc}{dt}) \times 10^{7}$ $ML^{-1}\ S^{-1}$
0	21.30	
2	17.72	
7	16.10	
15	14.16	
25	12.30	3.30
35	10.40	
45	8.60	
55	7.46	
65	7.00	

TABLE 6.4

[$KBrO_3$] = 1.00×10^{-3} M, [$HClO_4$] = 1.00×10^{-2} M

[Alanine] = 5.00×10^{-2} M, [Ir(III)] = 3.00×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (1.28×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ M L^{-1} s^{-1}
0	19.50	
2	17.74	
6	14.52	
12	12.36	
18	9.68	6.30
24	7.68	
30	6.82	
40	5.32	
50	4.40	

TABLE 6.5

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[Alanine] = 5.00 \times 10^{-2} M$, $[Ir(III)] = 3.80 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution (1.28×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\ L^{-1}\ S^{-1}$
0	19.50	
2	16.80	
4	14.84	
6	13.14	
10	9.76	8.06
15	7.80	
20	6.72	
25	5.68	
30	4.72	

TABLE 6.6

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[\text{Phenyl alanine}] = 5.00 \times 10^{-2}$ M, $[Ir(III)] = 0.38 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution (3.70×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ M L^{-1} S^{-1}
0	6.72	
5	5.82	
10	5.50	
25	5.18	0.58
50	4.76	
80	4.52	
110	4.20	
150	3.88	
200	3.00	

TABLE 6.7

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

[Phenyl alanine] $= 5.00 \times 10^{-2}$ M, $[Ir(III)] = 0.58 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.70×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	6.72	
5	5.50	
10	5.18	
25	4.56	
40	3.92	0.82
75	3.10	
125	2.50	
170	2.00	
225	1.48	

TABLE 6.8

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 1.00×10^{-2}M

[Phenyl alanine] = 5.00×10^{-2}M, [Ir(III)] = 0.76×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.70×10^{-3}M) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ $M\,L^{-1}\,s^{-1}$
0	6.72	
5	5.18	
10	4.80	
15	4.36	
20	3.96	1.16
25	3.50	
40	3.02	
55	2.46	
70	2.06	
100	1.08	

TABLE 6.9

[$KBrO_3$] = 1.00×10^{-3} M, [$HClO_4$] = 1.00×10^{-2} M

[Phenyl alanine] = 5.00×10^{-2} M, [Ir(III)] = 1.54×10^{-5} M

[$Hg(OAc)_2$] = 4.00×10^{-3} M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.70×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	6.72	
5	5.10	
10	4.26	
15	3.78	
20	3.24	
25	2.86	2.32
35	2.16	
50	1.90	
65	1.72	
80	1.58	

TABLE 6.10

$[KBrO_3]$ = 1.00×10^{-3}M, $[HClO_4]$ = 1.00×10^{-2}M

[Phenyl alanine] = 5.00×10^{-2}M, [Ir(III)] = 1.92×10^{-5}

$[Hg(OAc)_2]$ = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (2.22×10^{-3}M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0	11.20	
3	9.00	
8	7.60	
15	5.90	
25	4.36	2.92
40	3.70	
55	3.16	
70	2.40	
85	2.00	
100	1.68	

TABLE 6.11

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[\text{Valine}] = 3.34 \times 10^{-2}$ M, $[\text{Ir(III)}] = 0.24 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.75×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	6.74	
10	5.84	
20	5.60	
40	5.24	
60	5.00	
90	4.76	1.93
120	4.40	
180	3.88	
240	3.40	
300	3.00	

TABLE 6.12

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 1.00×10^{-2}M

[Valine] = 3.34×10^{-2}M, [Ir(III)] = 0.48×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

Time (min.)	Volume of hypo solution (3.75×10^{-3}M) in ml	$(\frac{-dc}{dt})\times10^{7}$ M L^{-1} s^{-1}
0	6.74	
5	5.86	
10	5.58	
20	5.26	
30	4.98	3.92
45	4.72	
60	4.42	
90	3.90	
120	3.38	
150	3.06	

TABLE 6.13

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[Valine] = 3.34\times10^{-3}M$, $[Ir(III)] = 0.96\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. 35°C

Time (min.)	Volumeeof hypo solution ($3.75\times10^{-3}M$) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ S^{-1}$
0	6.74	
3	5.82	
5	5.58	
10	5.26	
15	5.08	7.72
25	4.42	
40	3.90	
55	3.46	
70	3.12	
85	2.88	

TABLE 6.14

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[Valine] = 3.34\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. 35^0C

Time (min.)	Volume of hypo solution ($3.75\times10^{-3}M$) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}s^{-1}$
0	6.74	
3	5.80	
8	5.06	
12	4.46	15.28
20	3.92	
30	3.42	
40	3.00	
50	2.62	
60	2.34	

TABLE 6.15

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[Valine] = 3.34\times10^{-2}M$, $[Ir(III)] = 3.84 \times 10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. $35^{\circ}C$

Time (min.)	Volume of hypo solution ($3.60\times10^{-3}M$) in ml	$(-dc/dt) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0	7.48	
2	11.98	
5	10.44	
10	8.86	20.86
15	8.00	
20	7.02	
30	6.00	
40	5.08	
50	4.70	

The results of tables 6.1 - 6.5 and 4.4, tables 6.6 - 6.10 and 4.10 and tables 6.11 - 6.15 have been summarised in tables 6.16, 6.17 and 6.18, respectively.

TABLE 6.16

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[\text{Alanine}] = 5.00 \times 10^{-2}$ M, Temp. 35°C

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M

$[Ir(III)] \times 10^5$ M	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}	$k_1 \times 10^2 = \frac{(-dc/dt)}{[Ir(III)]}$ s^{-1}
0.78	1.64	2.10
1.35	2.85	2.11
1.55	3.30	2.13
1.92	4.08	2.12
3.00	6.30	2.10
3.80	8.06	2.12

Average value of $k_1 = 2.11 \times 10^{-2}$ s^{-1}

TABLE 6.17

$[KBrO_3] = 1.00\times10^{-3}$M, $[HClO_4] = 1.00\times10^{-2}$M

[phenyl alanine] = 5.00×10^{-2}M, Temp. 35^{o}C

$[Hg(OAc)_2] = 4.00\times10^{-3}$M

$[Ir(III)] \times 10^5$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}	$k_1 \times 10^2 = \frac{(-dc/dt)}{[Ir(III)]}$ s^{-1}
0.38	0.58	1.53
0.58	0.82	1.41
0.76	1.16	1.52
1.54	2.32	1.50
1.92	2.92	1.52
3.84	5.80	1.51

Average value of $k_1 = 1.50\times10^{-2}\,s^{-1}$

TABLE 6.18

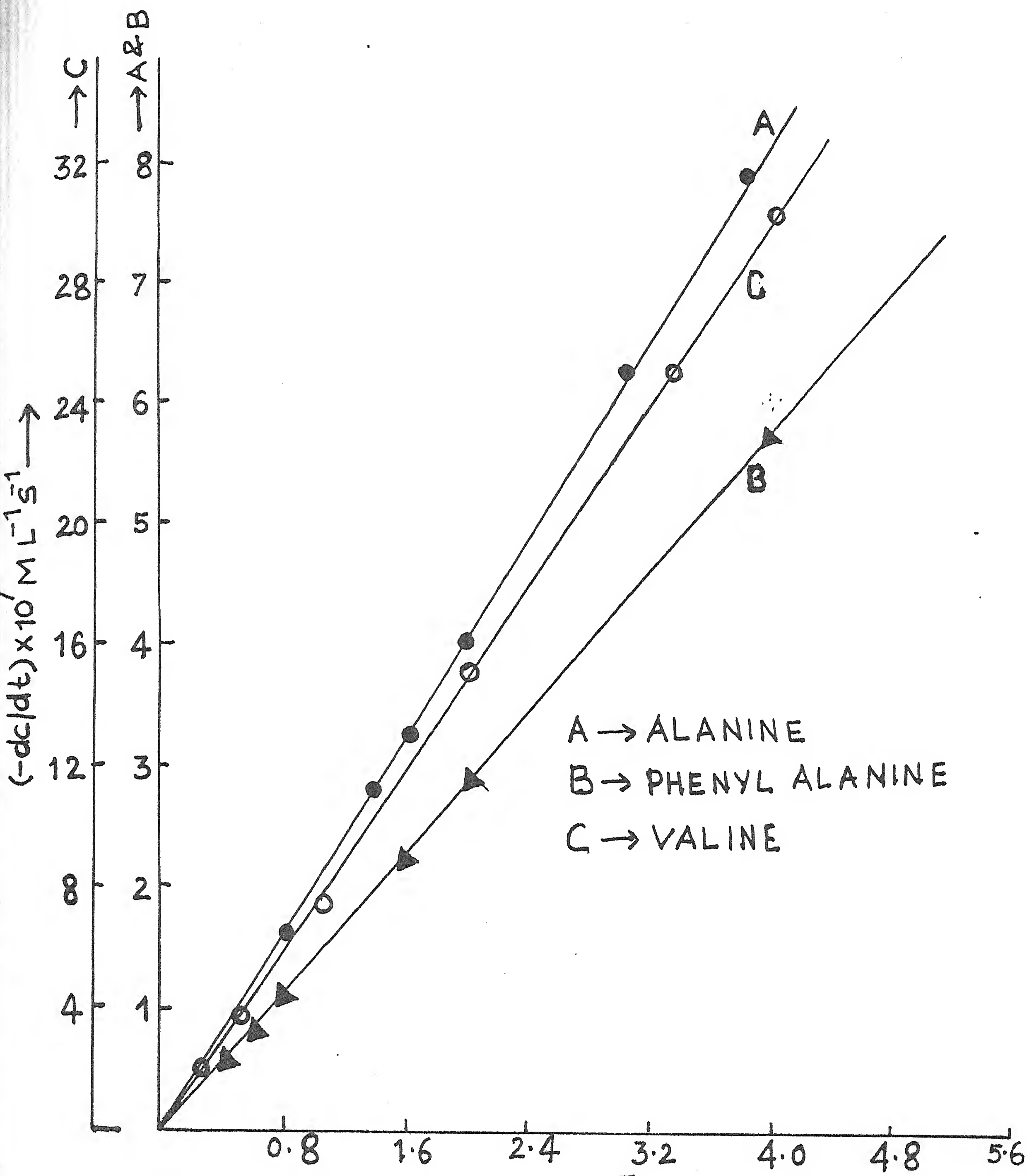
$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[Valine] = 3.34 \times 10^{-2}$ M, Temp. 35°C

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M

$[Ir(III)] \times 10^5$ M	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}	$k_1 \times 10^2 = \frac{(-dc/dt)}{[Ir(III)]}$ s^{-1}
0.24	1.93	8.04
0.48	3.92	8.17
0.96	7.72	8.04
1.92	15.28	7.96
3.84	30.86	8.03

Average value of k_1 = $8.04 \times 10^{-2} s^{-1}$



$[Ir(III)] \times 10^5 M \longrightarrow$

FIG. 6.1: EFFECT OF [Ir(III)] ON RATE AT 35°C. $[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$, $[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, $[ALANINE] = 5.00 \times 10^{-2} M$, $[PHENYL\ ALANINE] = 5.00 \times 10^{-2} M$ AND $[VALINE] = 3.34 \times 10^{-2} M$.

An examination of data of tables 6.16, 6.17 and 6.18 indicates that on increasing the concentration of iridium(III) chloride the value of $(-dc/_{dt})$ i.e. zero - order rate constant increases in direct proportionality, suggesting first order in iridium (III) chloride. First order dependence on Ir(III) is also obvious from nearly constant values of k_1 obtained at different concentrations of Ir(III).

The above experimental finding regarding order in Ir(III) is further, confirmed graphically (Fig.6.1). When $(-dc/_{dt})$ values are plotted against Ir(III) in oxidation of each of alanine, phenylalanine and valine, a straight line with slope equal to k_1 is observed. The graphical values of k_1 resembles well with average values of k_1 given in the bottom of each tables. This confirms first - order respect to Ir(III).

CHAPTER VII

EFFECT OF ADDITION OF MERCURIC ACETATE ON THE OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

7 : EFFECT OF ADDITION OF MERCURIC ACETATE ON THE OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

In this chapter an attempt has been made to study the effect of variation of concentration of mercuric acetate on the rate of oxidation of amino - acids used here. A series of experiments at different concentrations of mercuric acetate in oxidation of each of alanine, phenyl alanine and valine have been carried out at fixed concentrations of all other reactants. It has been observed that change in concentration of mercuric acetate did not bring about any change in the reaction velocity of oxidation of amino acids which is obvious from the summarised results recorded in the tables 7.1, 7.2 and 7.3 in oxidation of alanine, phenyl alanine and valine respectively.

TABLE 7.1

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[Alanine] = 3.32 \times 10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

Temp. 35°C

$[Hg(OAc)_2] \times 10^3 M$	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ S^{-1}$
1.00	3.26
1.50	3.28
2.00	3.31
2.50	3.30
3.00	3.25
3.50	3.27
4.00	3.28
5.00	3.26

TABLE 7.2

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[\text{Phenyl alanine}] = 5.00 \times 10^{-2}$ M, $[\text{Ir(III)}] = 1.92 \times 10^{-5}$ M

Temp. 35°C

$[Hg(OAc)_2] \times 10^3$ M	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
1.00	2.74
2.00	2.73
3.00	2.72
4.00	2.72
5.00	2.70
6.00	2.73
8.00	2.76
10.00	2.73

TABLE 7.3

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[Valine] = 3.34 \times 10^{-2} M$, $[Ir(III)] = 7.80 \times 10^{-6} M$

Temp. $35^{\circ}C$

$[Mg(OAc)_2] \times 10^3 M$	$(\frac{-dc}{dt}) \times 10^7$ $M L^{-1} S^{-1}$
1.00	9.12
2.00	9.09
3.00	9.10
4.00	9.10
5.00	9.11
6.00	9.12
8.00	9.10
10.00	9.09

It is evident from the results of tables 7.1 - 7.3 that reaction rate in any redox system is not influenced by change in the concentration of mercuric acetate. It also suggests that mercuric acetate here only functions here as bromide ions scavenger and in no other way it interferes with the reactions studied here. Thus by removing bromide ions, it eliminates possible bromine oxidation and thus ensures pure potassium bromate oxidation.

CHAPTER VIII

EFFECT OF VARIATION OF IONIC STRENGTH OF THE MEDIUM ON REACTION RATE

8 : EFFECT OF VARIATION OF IONIC STRENGTH OF THE MEDIUM ON REACTION RATE

Ionic strength variation effects helps in deciding the nature of the reactive species actually involved in the rate determining step. Therefore, it was thought worthwhile to investigate the effect of variation of ionic strength of the medium on the reaction velocity of the reactions involving amino acids as substrate and potassium bromate as oxidant. Hence in order to determine the effect of change of ionic strength (varied by addition of suitable amounts of sodium perchlorate), a series of experiments at different ionic strengths but under similar physical conditions of experiments have been performed and their results have been given in summarised form in tables 8.1, 8.2 and 8.3 for oxidation of alanine, phenylalanine and valine, respectively.

TABLE 8.1

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[\text{Alanine}] = 3.32\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. $35^{\circ}C$

$[NaClO_4] \times 10^2$ M	Ionic strength $(\mu)\times10^{-2}$M	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0.00	2.30	3.30
1.00	3.30	3.28
2.00	4.30	3.27
4.00	6.30	3.31
5.00	7.30	3.25
6.00	8.30	3.28
8.00	10.30	3.28
10.00	12.30	3.29
12.00	14.30	3.27

TABLE 8.2

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 1.00×10^{-2}M

[Phenyl Alanine] = 5.00×10^{-2}M, [Ir(III)] = 1.92×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. 35°C

[$NaClO_4$] x 10^2 M	Ionic strength $\mu \times 10^2$ M	($\frac{-dc}{dt}$) x 10^7 M L^{-1} s^{-1}
0.00	2.30	2.70
1.00	3.30	2.74
2.00	4.30	2.72
3.00	5.30	2.73
4.00	6.30	2.72
5.00	7.30	2.76
6.00	8.30	2.74
8.00	10.30	2.72
10.00	12.30	2.70
12.00	14.30	2.72

TABLE 8.3

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[Valine] = 3.34\times10^{-2}M$, $[Ir(III)] = 0.78\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. $35^{o}C$

$[NaClO_4] \times 10^2$ M	Ionic strength $\mu \times 10^2$ M	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0.00	2.30	9.08
1.00	3.30	9.10
2.00	4.30	9.06
3.00	5.30	9.12
4.00	6.30	9.10
5.00	7.30	9.11
6.00	8.30	9.12
8.00	10.30	9.10
10.00	12.30	9.08
12.00	14.30	9.10

A close examination of tables 8.1 - 8.3 clearly indicates that there is no significant effect of variation of ionic strength of the medium on rate of oxidation of alanine, phenylalanine and valine by acidic solution of potassium bromate. This conclusion drawn from experimental observations made in this chapter will be utilised while suggesting the reaction mechanism of aforesaid reactions catalysed by iridium (III) chloride.

CHAPTER IX

STUDY OF EFFECT OF ADDITION OF POTASSIUM CHLORIDE ON THE RATE OF OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

9 : STUDY OF EFFECT OF ADDITION OF POTASSIUM CHLORIDE ON THE RATE OF OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

In this chapter an attempt has been made to determine the effect of addition of potassium chloride on the rate of oxidation of alanine, phenylalanine and valine by acidic solution of potassium bromate in the presence of iridium(III) chloride. In order to realise the above aim, a set of experiments with varying amounts of potassium chloride under similar conditions of experiments were carried out and the results obtained were recorded in the consolidated form in Tables 9.1, 9.2 and 9.3 in oxidation of alanine, phenylalanine and valine, respectively.

TABLE 9.1

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[\text{Alanine}] = 2.50\times10^{-2}M$, $[Ir(III)] = 1.92\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. $35^{\circ}C$

$[KCl] \times 10^3 M$	$(\frac{-dc}{dt}) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0.00	1.96
1.00	1.98
1.50	1.96
2.00	1.97
2.50	2.00
3.00	1.97
4.00	1.96
5.00	1.98

TABLE 9.2

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[\text{Phenylalanine}] = 5.00 \times 10^{-2} M$, $[Ir(III)] = 3.84 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. 35°C

$[KCl] \times 10^{3} M$	$\left(\frac{-dc}{dt}\right) \times 10^{7}$ $M\,L^{-1}\,s^{-1}$
0.0Ø	5.79
1.00	5.80
1.50	5.82
2.00	5.78
2.50	5.80
3.00	5.81
4.00	5.82
5.00	5.80
6.00	5.79

TABLE 9.3

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[\text{Valine}] = 1.00 \times 10^{-2}$ M, $[\text{Ir(III)}] = 1.92 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 35°C

$[KCl] \times 10^3$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0.00	9.24
1.00	9.22
1.50	9.25
2.00	9.24
2.50	9.23
3.00	9.22
4.00	9.24
5.00	9.23
6.00	9.22

It is evident from the kinetic results of the summarised tables 9.1 - 9.3 that on increasing the concentration of potassium chloride the value of $(-dc/dt)$ is not significantly affected, which indicates that there is negligible effect of addition of potassium chloride on rate of oxidation of aforesaid amino acids by potassium bromate in the presence of acidic solution of iridium (III) chloride.

CHAPTER X

STUDY OF EFFECT OF TEMPERATURE ON THE VELOCITY OF Ir(III) CATALYSED OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

10 : STUDY OF EFFECT OF TEMPERATURE ON THE VELOCITY OF Ir(III) CATALYSED OXIDATION OF AMINO ACIDS BY POTASSIUM BROMATE

In previous chapters the title reactions have been studied in detail in order to compute the order of the reactions with respect to different reactants at 35°C. Here in this chapter an attempt would be made to study all the reactions at 30°, 40°, and 45°C. The kinetic results at these temperatures and at 35°C have been obtained under similar conditions of experiments and have been given respectively in tables 10.1 - 10.3, 10.4 - 10.6 and 10.7 - 10.9 for the oxidation of alanine, phenyl alanine and valine.

TABLE 10.1

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[\text{Alanine}] = 5.00\times10^{-2}M$, $[\text{Ir(III)}] = 1.92\times10^{-5}M$

$[\text{Hg(OAc)}_2] = 4.00\times10^{-3}M$, Temp. $30^{\circ}C$

Time (min.)	Volume of hypo solution ($2.59\times10^{-3}M$) in ml	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
0	9.64	
5	8.76	
10	8.42	
15	8.12	
25	7.68	2.80
35	7.22	
45	6.70	
60	6.41	
75	5.26	
90	4.42	

TABLE 10.2

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[\text{Alanine}] = 5.00 \times 10^{-2} M$, $[\text{Ir(III)}] = 1.92 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. $40^{\circ}C$

Time (min.)	Volume of hypo solution (2.59×10^{-3} M) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	9.64	
5	8.18	
10	7.70	
15	7.12	5.76
20	6.76	
30	5.50	
40	4.28	
50	3.50	
60	3.02	

TABLE 10.3

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[Alanine] = 5.00 \times 10^{-2} M$, $[Ir(III)] = 1.92 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$, Temp. $45^{\circ}C$

Time (min.)	Volume of hypo solution ($2.59 \times 10^{-3} M$) in ml	$(-\frac{dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	9.64	
2	8.24	
4	7.76	
6	7.42	8.66
8	7.18	
15	6.24	
25	4.44	
35	3.06	
45	2.02	

TABLE 10.4

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

[Phenylalanine] = 5.00×10^{-2} M, $[Ir(III)] = 3.84 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 30°C

Time (min.)	Volume of hypo solution (2.70×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} S^{-1}
0	9.24	
5	7.40	
10	5.90	
15	4.98	3.85
20	4.60	
25	4.32	
30	4.16	
50	3.60	

TABLE 10.5

[$KBrO_3$] = 1.00×10^{-3}M, [$HClO_4$] = 1.00×10^{-2}M

[Phenylalanine] = 5.00×10^{-2}M, [Ir(III)] = 3.84×10^{-5}M

[$Hg(OAc)_2$] = 4.00×10^{-3}M, Temp. $40^{o}C$

Time (min.)	Volume of hypo solution (2.70×10^{-3}M) in ml	$\left(\frac{-dc}{dt}\right)\times10^{7}$ M L^{-1} s^{-1}
0	9.24	
2	7.56	
4	6.64	
7	5.30	
10	4.32	7.90
15	3.86	
20	3.50	
25	3.24	
30	3.00	

TABLE 10.5

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[\text{Phenylalanine}] = 5.00\times10^{-2}M$, $[Ir(III)] = 3.84\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$, Temp. 45°C

Time (min.)	Volume of hypo solution ($2.70\times10^{-3}M$) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\ L^{-1}\ s^{-1}$
0	9.24	
2	7.32	
4	6.28	
6	5.24	13.48
10	3.84	
15	3.32	
20	2.80	
25	2.28	
30	1.96	

TABLE 10.7

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

[Valine] = 3.34×10^{-2} M, [Ir(III)] = 0.24×10^{-5} M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 30°C

Time (min.)	Volume of hypo solution (3.75×10^{-3} M) in ml	$(\frac{-dc}{dt}) \times 10^7$ $M\,L^{-1}\,s^{-1}$
0	6.74	
15	5.86	
30	5.68	
55	5.08	1.48
80	4.76	
105	4.34	
200	3.80	
300	3.38	

TABLE 10.8

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[Valine] = 3.34 \times 10^{-2}$ M, $[Ir(III)] = 0.24 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M, Temp. 40°C

Time (min.)	Volume of hypo solution (3.75×10^{-3} M) in ml	$\left(\frac{-dc}{dt}\right) \times 10^7$ M L^{-1} s^{-1}
0	6.74	
5	5.94	
10	5.72	
20	5.40	3.48
30	5.06	
45	4.72	
60	4.42	
90	3.90	

TABLE 10.9

$[KBrO_3] = 1.00 \times 10^{-3} M$, $[HClO_4] = 1.00 \times 10^{-2} M$

$[Valine] = 3.34 \times 10^{-2} M$, $[Ir(III)] = 0.24 \times 10^{-5} M$

$[Hg(OAc)_2] = 4.00 \times 10^{-3} M$ and Temp. $45^{o}C$

Time (min.)	Volume of hypo solution (3.75×10^{-3}M) in ml	$(\frac{-dc}{dt}) \times 10^7$ $ML^{-1}\ s^{-1}$
0	6.74	
5	5.82	
10	5.54	
15	5.36	4.46
20	5.16	
25	4.98	
30	4.82	
35	4.64	
40	4.36	

The results of tables 10.1 - 10.3 and table 4.4, tables 10.4 - 10.6 and table 4.10 and tables 10.7 - 10.9 and table 6.11 are consolidated in tables 10.10, 10.11 and 10.12 respectively.

TABLE 10.10

$[KBrO_3] = 1.00 \times 10^{-3}$M, $[HClO_4] = 1.00 \times 10^{-2}$M

[Alanine] = 5.00×10^{-2}M, [Ir(III)] = 1.92×10^{-5}M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$M

Temperature ^oC	$(\frac{-dc}{dt}) \times 10^7$ M L^{-1} s^{-1}
30	2.80
35	4.08
40	5.76
45	8.66

TABLE 10.11

$[KBrO_3] = 1.00\times10^{-3}M$, $[HClO_4] = 1.00\times10^{-2}M$

$[\text{Phenyl alanine}] = 5.00\times10^{-2}M$ $[Ir(III)] = 3.84\times10^{-5}M$

$[Hg(OAc)_2] = 4.00\times10^{-3}M$

Temperature $^{\circ}C$	$(-dc/dt)\times10^{7}$ $M\,L^{-1}\,s^{-1}$
30	3.85
35	5.80
40	7.90
45	13.48

TABLE 10.12

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M

$[\text{Valine}] = 3.34 \times 10^{-2}$ M, $[\text{Ir(III)}] = 0.24 \times 10^{-5}$ M

$[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M

Temperature $^\circ C$	$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}
30	1.42
35	1.98
40	3.42
45	4.46

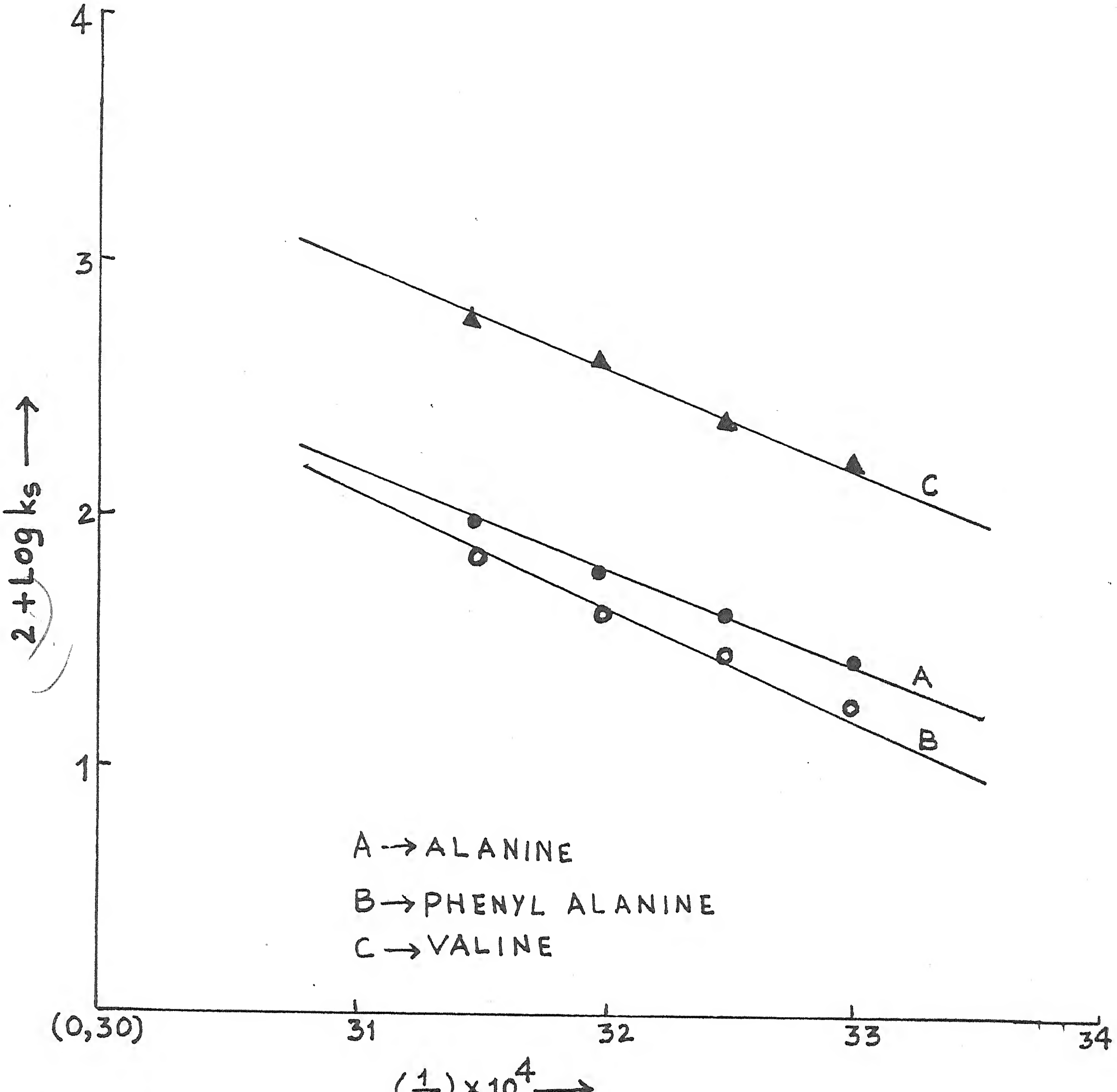


FIG. 10.1: PLOT BETWEEN LOG k_s AND (1/T)

$[KBrO_3] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M
[ALANINE] $= 5.00 \times 10^{-2}$ M, [PHENYL ALANINE] $= 5.00 \times 10^{-2}$ M,
[VALINE] $= 3.34 \times 10^{-2}$ M, [Ir(III)] $= 1.92 \times 10^{-5}$ M (A),
3.84×10^{-5} M (B) AND 0.24×10^{-5} M (C).

It is quite clear from the data of tables 10.10 - 10.12 that the oxidations of alanine, phenyl alanine and valine are influenced by an increase of temperature. In order to compute the thermodynamic parameters of these reactions, a graph between log ks and $\frac{1}{T}$ is plotted (Fig.10.1) where ks is specific rate constant. A straight line with slope equal to ($- E_a/_{2.303R}$) is obtained in each case and thus from the slope the value of Ea i.e. energy of activation is determined. The values of energy of activation for oxidation of alanine, phenyl alanine and valine are found as 19.71 K Cal/mole, 27.23 K cal/mole and 18.40 K cal/mole respectively. The value of Arrhenius frequency i.e. A in terms of log A is calculated as

$$\log A = \log ks + \frac{E\,a}{2.303\,R\,T} \qquad (1)$$

The value of entropy of activation i.e. $\Delta S^{\neq}$ is calculated by the formula (2)

$$\Delta S^{\neq} = 4.56 \log (A \times 10^{-13})$$

The value of free energy of activation i.e. ΔG is calculated by eqn (3)

$$\Delta G^{\neq} = \Delta H - T \Delta S^{\neq} \qquad (3)$$

$$\text{where} \quad \Delta H = E_a - RT$$

The values of k_s (specific rate constant), log A, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ have been given in the following table for oxidation of alanine, phenyl alanine and valine.

TABLE 10.13

Parameters	Alanine	Phenylalanine	Valine
ks (35°c)	45.50×10^{-2}	30.20×10^{-2}	2.41
E a	19.71 k k cal/mole	21.23 k cal/mole	18.40 k cal/mole
log A	13.54	14.46	13.37
$\Delta S^{\neq}$	2.48 e.u	6.72 e.u.	1.70 e.u.
$\Delta G^{\neq}$	18.95 k cal/mole	19.17 k cal/mole	17.38 k cal/mole

CHAPTER XI

RESULTS AND DISCUSSION

11 : This chapter describes the details of experimental observations made in previous chapters in iridium(III) chloride catalysed oxidation of alanine, phenyl alanine and valine by acidic solution of potassium bromate in the presence of mercuric acetate as bromide ion scavenger. It has been proved by preliminary investigations that reactions if carried out in the presence of mercuric acetate but in the absence of potassium bromate progress of reaction was found to be nil, suggesting that mercuric acetate is neither involved here as co - oxidant nor it is functioning as co - catalyst but it is only acting as Br^- scavenger. In the following section the results obtained are given in the summarised form.

In this chapter it is also intended to discuss the kinetic results and interpret them in order to propose the reaction mechanism which could give rate law capable of explaining all the observed experimental facts.

11.1 : SUMMARY OF KINETIC RESULTS OBTAINED IN I_r(III) CATALYSED OXIDATION OF AMINO ACIDS

Following are key results in the title reactions :

i) Zero - order dependence of all oxidations studied herewith respect to potassium bromate has been observed.

ii) First order kinetics with respect to each of alanine, phenyl alanine and valine was observed.

iii) Zero order with respect to H^+ in each case was observed.

iv) First-order with respect to iridium(III) chloride in oxidation of each amino acid was observed.

v) Negligible effect of addition of mercuric acetate on the reaction rate was observed.

vi) Zero effect of change in the ionic strength of the medium was observed in oxidation of each amino acid here.

vii) Successive addition of potassium chloride did not bring about any significant change in the rate of oxidation of amino acids investigated here.

viii) All reactions were observed to be susceptible to change in the temperature.

11.2 : REACTIVE SPECIES OF IRIDIUM(III) CHLORIDE IN ACIDIC MEDIA

It is worthwhile first to discuss the reactive species of iridium(III) chloride before the reaction mechanism is suggested. In excess of HCl, iridium (III) chloride exists[1] as $[IrCl_6]^{3-}$ which forms various species viz. $[IrH_2O\,Cl_5]^{2-}$, $[IrCl_4(H_2O)_2]^{1-}$ and $[Ir(H_2O)_3\,Cl_3]$ in aqueous solutions. These species may be considered in equilibrium as follows :

$$[IrCl_6]^{3-} \rightleftharpoons [IrCl_5]^{2-} + Cl^- \qquad (i)$$

$$[IrCl_5]^{2-} \rightleftharpoons [IrCl_4]^{1-} + Cl^- \qquad (ii)$$

$$[IrCl_4]^{1-} \rightleftharpoons IrCl_3 + Cl^- \qquad (iii)$$

A negative effect of Cl^- on the rate of reaction during present studies suggests $[IrCl_3]$ as the

reactive species of the catalyst. Ir(III) catalysed oxidation of organic compounds in acidic medium has also been explained[2] by considering $IrCl_3$ as the reactive species of the catalyst.

Here in present case negligible effect of Cl^- on the reaction rate suggests involvement of neutral species $[IrCl_3(H_2O)_3]$ as reactive species of iridium (III) chloride in acidic medium. For the sake of convenience Ir(III) has been written for $[IrCl_3(H_2O)]$ in all following steps.

11.3 : NATURE OF OXIDISING SPECIES OF POTASSIUM BROMATE IN ACIDIC MEDIUM

Potassium bromate is a strong electrolyte which gives bromate ions as given below in aqueous solution

$$KBrO_3 \rightleftharpoons K^+ + BrO_3^- \qquad (i)$$

Bromate ions thus present in the aqueous solution takes up a proton[3] to form $HBrO_3$ as given by eqn (ii)

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3 \qquad (ii)$$

Thus in acidic solution potassium bromate participates in the reaction in the form of $HBrO_3$.

11.4 : MECHANISM OF Ir(III) CATALYSED OXIDATION OF ALANINE, PHENYL ALANINE AND VALINE BY ACIDIC SOLUTION OF POTASSIUM BROMATE

It has been concluded that in oxidation of the title reducing amino acids the reaction is zero - order with respect to potassium bromate i.e. oxidant, first - order in amino acids and first - order in iridium(III) chloride. These kinetic data clearly indicate that potassium bromate or its reactive species $HBrO_3$ is involved in a fast step after rate determining slow step. It has been also concluded in section 11.2 that in acidic medium iridium(III) chloride participates in the catalysis in neutral form $[IrCl_3(H_2O)_3]$ which has been represented here as Ir(III) for the sake of convenience.

Thus following steps are suggested on the basis of kinetic results reported in section 11.1 and on the basis of reactive species of iridium(III) chloride and potassium bromate expressed in section 11.2 and section 11.3 respectively.

$$BrO_3^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HBrO_3 \qquad (I)$$

$$Ir(III) + AA \overset{K_2}{\rightleftharpoons} [Ir(III) \cdot A\,A] \qquad (II)$$

$$(C_1) \qquad\qquad (C_2)$$

$$[Ir(III) \cdot A\,A] + H_2O \xrightarrow{k} [Ir(III)\ A\,A]^{1-} + H^+ \qquad (III)$$

$$(C_2) \quad \text{Slow} \qquad (X)$$

$$(X) + HBrO_3 \xrightarrow{fast} HBrO_2 + Ir(III) + \text{Products} \qquad (IV)$$

The rate of the reaction in terms of loss of potassium bromate concentration may be expressed as eqn (1)

$$\frac{-d[BrO_3^-]}{dt} = k\ [C_2] \qquad (1)$$

On applying steady state treatment to $[C_2]$ we have

$$\frac{d\,[C_2]}{dt} = k_1\,[C_1][A\,A] - k_{-1}\,[C_2] - k\,[C_2][H_2O]$$

$$\text{or} \quad k_{-1}[C_2] + k[C_2][H_2O] = k_1[C_1][A\ A]$$

$$\text{or} \quad [C_2] = \frac{k_1[C_1][A\ A]}{k_{-1} + k[H_2O]} \tag{2}$$

Thus from eqn (1) and (2) we have

$$\frac{-d[BrO_3^-]}{dt} = \frac{k\,k_1[C_1][A\ A][H_2O]}{k_{-1} + k[H_2O]} \tag{3}$$

Again total concentration of iridium (III) chloride may be written as eqn (4) from steps II & III.

$$[Ir(III)]_T = [C_1] + [C_2] \tag{4}$$

Comparing eqns (2) and (4)

$$[Ir(III)]_T = [C_1] + \frac{k_1[C_1][A\ A]}{k_{-1} + k[H_2O]}$$

$$[Ir(III)]_T = [C_1]\left\{1 + \frac{k_1[A\ A]}{k_{-1} + k[H_2O]}\right\}$$

$$[Ir(III)]_T = [C_1]\left\{\frac{k_{-1} + k[H_2O] + k_1[A\,A]}{k_{-1} + k[H_2O]}\right.$$

$$\text{or } [C_1] = \frac{[Ir(III)]_T\,(k_{-1} + k[H_2O])}{k_{-1} + k[H_2O] + k_1[A\,A]} \qquad (5)$$

On substituting the value of $[C_1]$ from eqn (5) in eqn (3) we have

$$\frac{-d[BrO_3^-]}{dt} = \frac{k\,k_1[A\,A][H_2O]\,[Ir(III)]_T\,(k_{-1} + k[H_2O])}{(k_{-1} + k[H_2O])\,(k_{-1} + k[H_2O] + k_1[A\,A])}$$

$$\text{or } \frac{-d[BrO_3^-]}{dt} = \frac{k\,k_1[A\,A][Ir(III)]_T[H_2O]}{k[H_2O] + k_{-1} + k_1[A\,A]} \qquad (6)$$

On assuming further

$$k\left[H_2O\right] \gg k_{-1} + k_1 \left[A\ A\right], \qquad \text{we have}$$

$$\frac{-\,d\left[BrO_3^-\right]}{dt} = \frac{k\,k_{-1}\left[A\ A\right]\left[Ir(III)\right]_T\left[H_2O\right]}{k\left[H_2O\right]}$$

or

$$\frac{-d\left[BrO_3^-\right]}{dt} = k_1 \left[A\ A\right]\left[Ir(III)\right]_T \qquad (7)$$

The rate law (7) explains the observed kinetics. Hence the proposed mechanism is valid.

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